Amine-Containing Nanoporous Materials for CO_2 Removal

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ABSTRACT

Capture of CO_2 was investigated using both amine-grafted and polyethylenimine(PEI)-impregnated nanoporous silica. Grafted materials were synthesized using pore-expanded MCM-41 silica (PE-MCM-41) as support; whereas in addition to PE-MCM-41, impregnated materials used a series of SBA-15 silicas with different pore lengths and sizes. This work summarizes our multifaceted studies dealing with the following issues (i) importance of the pore size, volume and length, (ii) optimization of amine-grafting conditions, (iii) CO_2 adsorption capacity and rate, (iv) selectivity toward CO_2 vs. other adsorbates such as N_2, O_2, H_2, CH_4, H_2S, and SO_2, (v) adsorption-desorption cycling, (vi) stability of the adsorbent in the presence of moisture, (vii) dry CO_2-induced deactivation and mitigation thereof, and (viii) oxidative degradation.

INTRODUCTION

Amine-containing nanoporous materials gained tremendous popularity in recent years as adsorbents for CO_2 removal [1]. When properly designed, amine-functionalized materials exhibit high adsorption capacity, fast CO_2 adsorption and desorption, and low-energy requirements for recycling compared to amine solutions [1,2]. Although work in this area has been extensive in the past few years, the literature is dominated by measurements of equilibrium and near equilibrium CO_2 uptake using simple gas mixtures, without the typical impurities found in industrial gases. However, in addition to CO_2 uptake and adsorption-desorption kinetics, the stability of the materials is a critical property with direct impact on their lifetime, thus on the economics of any commercial-scale operation. The stability of amine-containing adsorbents is a complex issue associated with both physical conditions such as temperature, pressure and time, and chemical factors such as the interaction of the adsorbent with different species in the gas feed, including CO_2. The effects of a variety of common gaseous impurities such as water vapor [3], SO_2[4], H_2S[5], and O_2[6] on amine-containing materials were investigated to different degrees of depth. The current contribution will provide an overview of our work and others on the properties and stability of amine-containing adsorbents.

RESULTS AND DISCUSSION

Figure 1 lists all the aminosilanes and polyamines used for grafting and impregnation of mesoporous materials, respectively. As reported elsewhere [7], aminosilanes were grafted on a pore-expanded MCM-41 silica whose surface area, pore volume and pore size were 1153 m^2/g; 2.81 cm^3/g and 11.0 nm [8]. Linear and branched polyethylenimine (PEI) as well as polyallylamine were loaded on PE-MCM-41 and different SBA-15 mesoporous silicas. The synthesis of the mesoporous supports has been reported elsewhere [9]. The pore length of the supports was as follows: 25 μm for PE-MCM-41, 2.5 μm for SBA-15LP and SBA-15SP, where LP and SP stand for large (10.5 nm) and small (7.2 nm) pores, respectively, and 0.2 μm for SBA-15PLT, where PLT means platelets.
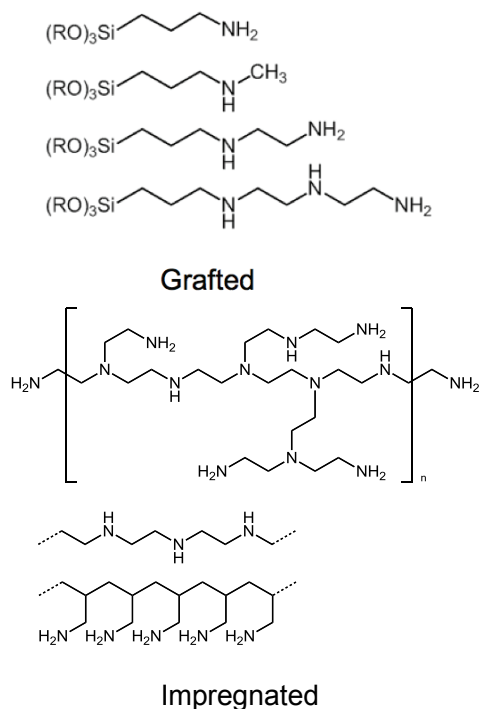

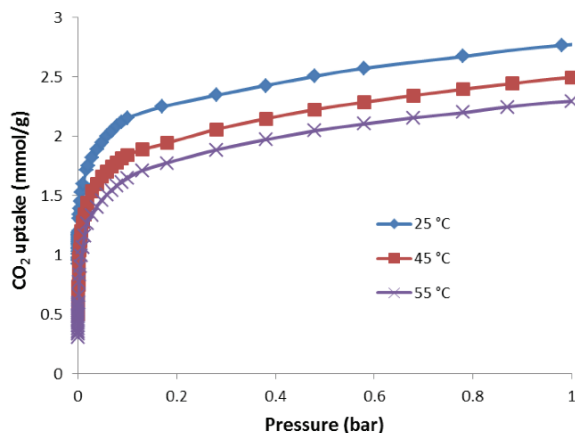Figure 1. Grafted and impregnated amines used for CO_2 capture.

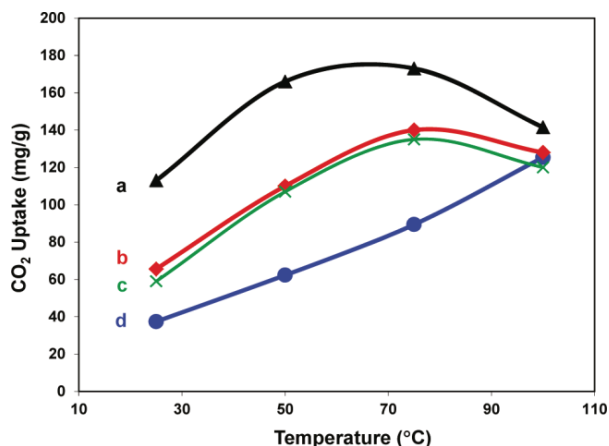Figure 2. CO_2 adsorption isotherms over triamine-grafted PE-MCM-41.

Figure 3. CO_2 uptake for (a) SBA-15PLT(55), (b) SBA-15LP(50%), (c) SBA-15SP(50%), and (d) PE-MCM-41(55) at different temperatures after 180 min of exposure to pure CO_2.

Due to the exothermic nature of CO_2 adsorption, all grafted amines showed the expected decreasing adsorption capacity as the temperature increased (Figure 2). However, impregnated PEI materials were dominated by diffusion resistance. Depending on the PEI loading, the CO_2 uptake exhibited a maximum, typically in the range of 50 to 80 °C (Figure 3). The diffusion resistance was successfully mitigated by decreasing the diffusion path length using mesoporous platelets with very short pores [10]. Figure 3 shows the CO_2 uptake for PE-MCM-41(55), SBA-15LP(50), SBA-15SP(50), and SBA-15PLT(55) in the presence of pure CO_2 at different temperatures after 180 min of exposure. The number in parentheses is the PEI (Mw = 600) loading. PEI-modified conventional SBA-15 (traces b and c) with different pore diameters, i.e., 7.2 and 10.5 nm, exhibited the same CO_2 uptake. Therefore, the effect of the pore diameter can be neglected for materials with completely filled pores. This indicates that the changes in CO_2 uptakes shown in Figure 3 are directly associated with the pore length. Figure 3 shows that, up to ca. 90 °C, the shorter the pore length, the higher the CO_2 uptake. In particular, SBA-15PLT(55) outperformed all three other adsorbents at all temperatures. Although SBA-15PLT had a lower surface area and pore volume than PE-MCM-41 (746 vs. 1254 m^2/g and 1.40 vs. 2.44 cm^3/g), SBA-15PLT(55) exhibited a much higher CO_2 uptake than PE-MCM-41(55). For instance, at 50 °C, the CO_2 working capacity for the SBA-15PLT-based adsorbent was 2.7 and 1.45 times higher than its PE-MCM-41 and SBA-15LP counterparts, respectively. It is likely that SBA-15PLT(x) adsorbents, with the shortest diffusion pathway, exhibit higher amine accessibility with diminished diffusion resistance, leading to higher CO_2 uptake. On the contrary, in materials with longer pore channels, such as PE-MCM-41 and conventional SBA-15, there is stronger diffusion resistance, giving rise to lower CO_2 uptake.

In the presence of dry CO_2-containing feed gas, all materials with the exception of grafted *N*-methyl-propylamine, deactivated at different rates depending on the severity of the adsorption and desorption conditions. Using adsorption measurements in conjunction with ^{13}C NMR and in-situ infrared spectroscopy, the deactivation was demonstrated to be associated with the gradual loss of amine groups via the formation of urea linkages [11]. Figure 4 summarizes all the pathways associated with CO_2-induced deactivation.

Oxygen is another ubiquitous impurity in CO_2-containing gases such as flue gas and biogas, with concentrations ranging from 3 to 10%. There is also a strong interest to remove CO_2 from air (21% O_2) using amine-containing adsorbents. Therefore, it is essential to investigate the effect of oxygen at different temperatures and concentrations on the adsorption of CO_2 by amine-containing materials. Previous studies [6] used ^{13}C NMR, N(1s) XPS, FTIR and FT-Raman directly on a variety of air-deactivated adsorbents, including grafted amines and impregnated polyamines. However, because of the limited resolution of such techniques applied to surface species, no detailed picture of the oxidative degradation pathways of supported amines has emerged. Here, we developed a solvent extraction procedure to remove surface species, and used a variety of 1D and 2D NMR techniques, including ^{29}Si, ^{13}C, ^{1}H, ^{1}H-^{15}N HMBC, ^{1}H-^{13}C HMQC, COSY and DOSY to delineate the nature of amine oxidized species. ^{13}C NMR and ^{13}C DEPT spectra of a solution of air-deactivated adsorbent show new CH_2 species (10-60 ppm) as well as a series of oxidized carbon with (-CH=N-) and without (-CO-) hydrogen (158-173 ppm). Combining information from different NMR spectra, several structural units were conclusively established.

Mechanism A: Formation of open-chain ureas
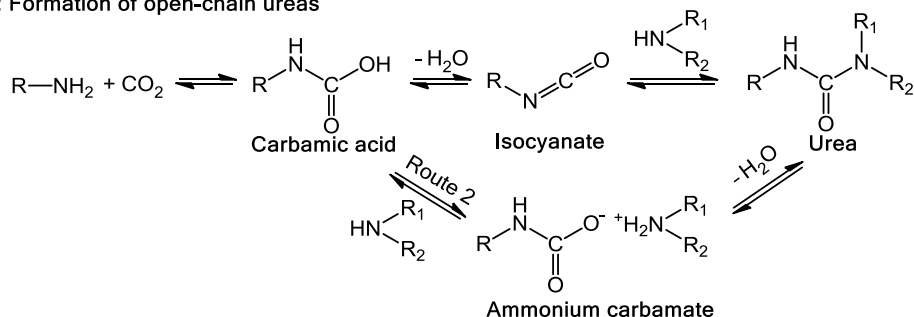
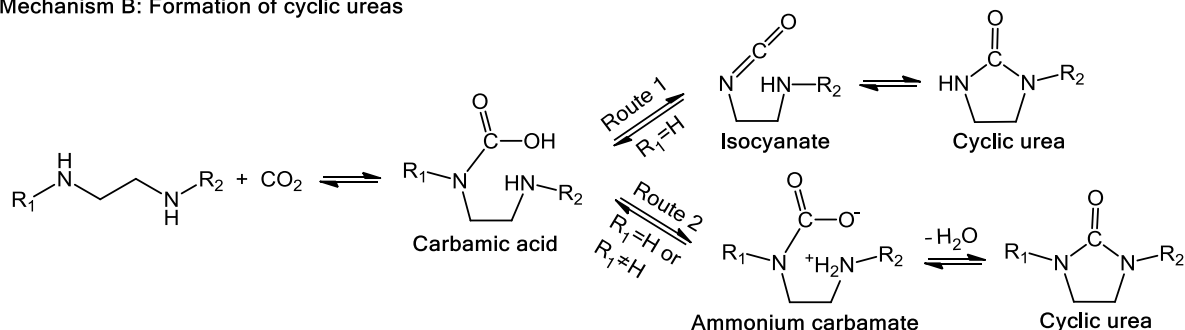**Mechanism B: Formation of cyclic ureas**

Figure 4. Pathways associated with CO_2-induced deactivation [11].

In conclusion, this work dealt with a variety of amine-containing CO_2 adsorbents. It involved in depth investigation of their equilibrium and kinetic behavior as well their selectivity, stability and deactivation processes.

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